

## Herbicide Dissipation from Low Density Polyethylene Mulch

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Field and laboratory studies were conducted to examine herbicide dissipation when applied to low density polyethylene (LDPE) mulch for dry scenarios vs. irrigation. Analytical chemical analysis was used for quantification. In field studies, halosulfuron, paraquat, carfentrazone, glyphosate, and flumioxazin were surface applied to black 32- $\mu$ m-thick (1.25 mil) LDPE mulch. LDPE mulch harvest began 1 h after treatment (HAT) then continued every 24 h for five consecutive rain-free days after treatment (DAT) to determine the level of herbicide dissipation from the LDPE mulch surface. In a related study, treated LDPE mulch was harvested 1 HAT, then sprinkler irrigation was applied, followed by a sampling five HAT, then the same irrigation and sampling procedure was repeated every 24 h for five consecutive DAT. The order for half-life, as defined as time for 50% dissipation ( $DT_{50}$ ), varied by herbicide and method of dissipation for dry and irrigated studies. Data indicated that glyphosate and paraquat dissipation was rapid following irrigation. Glyphosate and paraquat  $DT_{50}$  were both 1 h in the irrigated study, but 84 and 32 h for the dry scenario, respectively. This indicated that glyphosate and paraquat could be removed from LDPE mulch with rainfall or irrigation, primarily due to their high water solubility. Halosulfuron and flumioxazin  $DT_{50}$  were 3 and 6 h in the irrigated study, and 18 and 57 h for the dry study, respectively. Carfentrazone  $DT_{50}$  was similar at 28 and 30 h for the irrigated and dry studies, respectively. This indicated that carfentrazone was adsorbed to the LDPE mulch, and irrigation water did not remove it from the LDPE mulch. Results from  $^{14}$ C-herbicide laboratory studies were similar to those from field studies for halosulfuron, glyphosate, paraquat, and flumioxazin.

**Nomenclature:** Carfentrazone; flumioxazin; glyphosate; halosulfuron; paraquat.

**Key words:** Herbicide persistence, herbicide dissipation, low density polyethylene mulch, exponential decay equation, half-life.

The use of LDPE mulch when fumigating to manage weeds, diseases, and nematodes has become the standard for production of many vegetables in the southeastern United States (Grey et al. 2007; Johnson and Mullinex 2005; Patterson 1998; Webster et al. 2001). In Georgia, at least three crops are grown following a single fumigation and installation of mulch. Producing multiple crops before removing the mulch is done in order to minimize expenses associated with the fumigant, mulch, and drip tape irrigation by distributing these costs over multiple crops. Succeeding vegetable crops are transplanted directly into the existing LDPE covered beds. Producers apply herbicides between crop plantings in order to destroy the previous crop or weed infestations (Gilreath et al. 2006). Unfortunately, numerous herbicides applied over-the-top of LDPE mulch can leave residues on the mulch that may injure crops that are transplanted soon afterwards (Gilreath and Durancieu 1986; MacRae and Culpepper 2007).

LDPE mulch is manufactured as a petroleum-based thermoplastic containing black carbon (Nerin et al. 1996). LDPE mulch has permeability to fumigants via diffusion through the film matrix (Papiernik and Yates 2001a, 2001b). This occurs as the fumigant dissolves into the surface of the LDPE mulch facing the soil, diffuses through the film, and eventually evaporates from the opposite surface (Rogers 1985).

The persistence and dissipation of paraquat from LDPE mulch has been evaluated using bioassays (Gilreath and Durancieu 1986) and a colorimetric procedure (Gilreath et al. 2006). Previous research noted that paraquat dissipation from LDPE mulch was achieved by photo degradation or removal

with an eluant such as water. In bioassay studies, glyphosate did not photo degrade, but could be eluted with water (Gilreath and Santos 2004). Chlorothalonil, chlorpyrifos, and - and  $\beta$ -endosulfan absorption to black LDPE mulch were all less than 5% after 3 d of exposure (Nerin et al. 1996). Nerin et al. (1996) concluded that pesticide absorption to LDPE mulch (into the matrix) was a kinetically slow process requiring, in some instances, greater than 7 d to reach maximum absorption. These same authors also stated that lipo-solubility of the pesticide affected absorption, and that when absorbed to LDPE mulch, pesticides had great stability and did not spontaneously degrade. Rice et al. (2001) confirmed the runoff losses of chlorothalonil and  $\beta$ -endosulfan from polyethylene mulch.

Understanding the impact of dissipation of herbicides from LDPE mulch will establish which herbicides producers will utilize between vegetable crop plantings. The objective of this research was to directly compare the dissipation of glyphosate, paraquat, halosulfuron, carfentrazone, and flumioxazin from LDPE mulch using field experiments and analytical chemical analysis. Additional laboratory experiments utilized  $^{14}$ C-radiolabeled glyphosate, flumioxazin, halosulfuron, and paraquat to quantify sorption and dissipation.

### Materials and Methods

Field studies were conducted in Ty Ty, GA to evaluate the dissipation of herbicides from LDPE mulch. For all field experiments, herbicide dissipation was measured quantitatively using analytical techniques for two scenarios: under dry conditions (rain free and no irrigation) vs. irrigation at regular intervals using water as an eluant. Soil preparation for LDPE mulch included moldboard plowing and disk harrowing to remove all plant residues. Soil was Tifton loamy sand (fine-loamy, kaolinitic, thermic Plinthic Kandiudults) with 86% sand, 8% silt, 6% clay, organic matter range of 0.5 to 1.5%, and pH range of 6.0 to 6.9. Bed formation (20-cm raised

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Table 1. Environmental data for herbicide dissipation experiments at Ty Ty, GA.

Experiment							
Dry				Irrigated			
Date	Temperature		Radiation	Date	Temperature		Radiation
	Max	Min	MJ <sup>a</sup> m <sup>-2</sup>		Max	Min	MJ m <sup>-2</sup>
Oct 1, 2003	25	—	21	Dec 8, 2003	16	—	11
Oct 2, 2003	24	11	22	Dec 9, 2003	20	4	3
Oct 3, 2003	28	11	21	Dec 10, 2003	17	5	5
Oct 4, 2003	28	13	20	Dec 11, 2003	11	4	10
Oct , 2003	28	14	20	Dec 12, 2003	15	2	13
Oct 6, 2003	29	18	14	Dec 13, 2003	15	5	13
Total			118				55
Feb 28, 2004	16	—	19	Mar 15, 2004	23	—	11
Feb 29, 2004	21	4	18	Mar 16, 2004	22	16	8
Mar 1, 2004	23	15	8	Mar 17, 2004	21	8	23
Mar 2, 2004	22	13	16	Mar 18, 2004	25	7	22
Mar 3, 2004	26	13	16	Mar 19, 2004	28	12	22
Mar 4, 2004	25	17	16	Mar 20, 2004	28	13	22
Total			93				108

<sup>a</sup> Abbreviation: MJ, megajoules light.

bed), fumigation with methyl bromide (258 kg ai ha<sup>-1</sup>) plus chloropicrin (133 kg) and laying of 32- $\mu$ m-thick (1.25 mil) LDPE mulch<sup>1</sup> occurred simultaneously with a super bedder plastic layer. Individual plots constituted a single bed, 0.8 m wide by 6 m long.

Experiments were conducted from 2003 to 2004. For these experiments, herbicide treatments included paraquat<sup>2</sup> at 1,264 g ai ha<sup>-1</sup>, glyphosate<sup>3</sup> (potassium salt of glyphosate formulation) at 1,955 g ae ha<sup>-1</sup>, carfentrazone<sup>4</sup> at 80 g ai ha<sup>-1</sup>, halosulfuron<sup>5</sup> at 53 g ai ha<sup>-1</sup> and flumioxazin<sup>6</sup> at 54 g ai ha<sup>-1</sup> applied with a Teejet 11002 flat-fan nozzle.<sup>7</sup> Herbicide application dates were October 1, 2003 and March 2, 2004 for the dry studies, and December 8, 2003 and March 15, 2004 for the irrigated studies. Maximum and minimum temperatures and total daily solar radiation were recorded (Table 1) (Hoogenboom 2008).

For all field experiments, herbicides were applied with a CO<sub>2</sub>-pressurized backpack sprayer calibrated to deliver 140 L ha<sup>-1</sup> at 150 kPa. Each test used a randomized complete block with treatments replicated four times. LDPE mulch samples were collected at 1, 24, 48, 72, 96, and 120 HAT for the dry studies. The dry experiments did not receive irrigation or rainfall. For the irrigated experiments, samples were collected at 1 HAT, irrigated at 3 HAT with 1 cm of water using an overhead irrigation system, then sampled at 5 HAT. This washing and sampling procedure was then repeated at 24, 48, 72, and 96 HAT. Irrigation water pH samples were periodically collected and ranged from 7.0 to 8.1.

Samples were collected from each plot using an open faced wooden square frame with an inside area of 0.1 m<sup>2</sup>. A box-cutting knife was used to harvest the LDPE mulch along the inside edge of the square. Needle-nosed pliers were then used to mechanically fold the LDPE mulch inwardly to prevent contact of the treated surface with any foreign objects. Samples were then carefully stored in brown glass jars.<sup>8</sup> For all studies, care was taken to prevent contamination between samples and to collect a representative sample from each plot. All samples were immediately frozen by placing in a cooler of dry ice upon collection and then stored at -10 C until analysis.

Field plot replicate sample integrity was maintained throughout sample collection, preparation, and chemical analysis. For herbicide analysis, samples were removed from the freezer. All extractions were done with a mixture of 20 to 50% methanol<sup>9</sup> with high performance liquid chromatography (HPLC) grade water,<sup>9</sup> depending on the polarity of the herbicide. The extraction volumes were 200 ml for the initial treatment day concentrations and were reduced to 100 ml for lower concentration post wash samples. Samples with higher concentrations were diluted to maintain instrumental column and detector load capabilities, and these factors were figured into final quantitative analyses. Samples were shaken on a reciprocating shaker for 45 min and then centrifuged at 4500 rpm for 30 min. Samples were then passed through a 0.45  $\mu$ M polytetrafluoroethylene (PTFE) membrane filter<sup>9</sup> that was fitted with a leur-lock syringe,<sup>9</sup> and then passed into injection vials.<sup>9</sup> A Waters Alliance 2690 system<sup>10</sup> coupled to a Waters Micromass Quatro<sup>10</sup> (MS) triple quadrupole mass spectrometer was used to analyze the samples using electrospray ionization using standard curves generated from technical materials for each herbicide. Since the HPLC was linked to the MS, no analytical measures (wavelengths) were taken as the sample passed from one system to the other.

Analytical methods, mobile phase, columns, flow rates, ions monitoring settings, cone voltage, and desolvation temperature and gas settings are described for each herbicide in Table 2. Data were processed using Waters Masslynx software.<sup>10</sup>

For all measurements, ANOVA was applied to the data combined across herbicide and timing of experiment to test for interactions. Regression analysis was performed using SAS nonlinear regression. The intent was to determine if the response could be described by using the exponential decay equation

$$y = B_0 e^{-B_1(x)} \quad [1]$$

where  $y$  is herbicide concentration,  $B_0$  is the initial concentration,  $B_1$  is dissipation rate, and  $x$  is time in HAT. After the data was regressed against time in hours, the output from the analysis included the first-order-dissipation rate constant ( $k$ ) (Ohmes et al. 2000). Data for dry vs. irrigation exponential decay equations were subjected to ANOVA using

Table 2. Analytical methods, mobile phase, columns, flow rates, ions monitoring settings, cone voltage, and desolvation temperature and gas settings for herbicides evaluated in dry and wash off studies from low density polyethylene mulch studies.

Herbicide	Analytical method	Mobile phase	Column	Flow rate ml min <sup>-1</sup>	Ion monitoring	Cone voltage C	APCI/ESI
Glyphosate	LC – MS SIR <sup>a</sup>	ACN 50 mM ammonium acetate	Phenomenex C18	0.7	APCI positive	100	475
Paraquat	LC – MS SIR	60:40 ACN Buffer pH 4.5	Water Si	0.4	ESI negative	41	380
Halosulfuron	LC – MS SIR	ACN 10% MeOH with 0.1 ml ammonium hydroxide	YMC ODS	0.2	ESI negative	32	370
Carfentrazone	LC – MS SIR	ACN 10 MeOH with 10 mM formic acid	YMC ODS	0.2	ESI positive	23	350
Flumioxazin	LC – MS MRM	ACN 1.25 mM TDFHA	Hypersil ODS	0.6	APCI positive	40	484

<sup>a</sup> Abbreviations: SIR, single ion recording method; MRM, multiple reaction monitoring; TDFHA, tridecafluoropentanoic acid; ACN, acetonitrile; LC-MS, liquid chromatography-mass spectrometry; ESI, electrospray ionization; APCI, atmospheric pressure, chemical ionization; ODS, octadecyl silane.

the general linear models procedures with mean separation using 95% asymptotic confidence intervals.

Dissipation time (50%) was then determined using the equation

$$DT_{50} = \ln 0.50 / k \quad [2]$$

(Dermiyati and Yamamoto 1997; Mueller et al. 1999). Data were then graphed using SigmaPlot 8.0.<sup>11</sup>

Glyphosate, flumioxazin, halosulfuron, and paraquat were applied to 0.05-m<sup>2</sup> black 1.25-mil polyethylene mulch, similar to that used for the field studies along with <sup>14</sup>C-labeled materials. Solutions were prepared by mixing radio-labeled materials with the previously described herbicides. These included <sup>14</sup>C-glyphosate<sup>12</sup> (glycine 2-<sup>14</sup>C labeled with 0.27 GBq mmol<sup>-1</sup> specific activity, radiochemical purity > 98%), <sup>14</sup>C-paraquat<sup>13</sup> (methyl <sup>14</sup>C labeled with 1.2 GBq mmol<sup>-1</sup> with radiochemical purity > 98%), <sup>14</sup>C-flumioxazin<sup>14</sup> (ring labeled 12.9 MBq mg<sup>-1</sup> with radiochemical purity > 99%), and <sup>14</sup>C-halosulfuron<sup>15</sup> (ring labeled specific radioactivity = 1,162 MBq mmole<sup>-1</sup>, and radio purity > 98%). Radioactivity varied by herbicide ranging from 33 to 250 Bq µl<sup>-1</sup>. Glyphosate and flumioxazin were both applied at 3 and 11 ppm while paraquat and halosulfuron were applied at 0.5 and 3 ppm, respectively. All herbicides were evaluated at 20 and 30 C in controlled environment chambers with no supplemental light. Treated polyethylene mulch was rinsed with water at 6, 24, 48, and 96 h after treatment to determine amount of herbicide remaining on polyethylene mulch and the amount that could be removed. Distilled water (2 ml) was applied across the surface of the LDPE mulch and collected in 20-ml borosilicate glass liquid scintillation vials.<sup>9</sup> Fifteen ml of liquid scintillation fluid<sup>16</sup> was added to each vial and radioactivity was determined via liquid scintillation spectroscopy.<sup>17</sup> Experiments were arranged in a completely randomized design and repeated in time. Data were subjected to ANOVA and tested for interactions. Treatment means were separated by Fisher's Protected LSD test at P ≤ 0.05.

## Results and Discussion

There were no detectable herbicide by experiment interactions so data for herbicide by time of experiment were combined for presentation. There were differences for environmental measures taken during the course of each experiment (Table 1). However, all experiments were conducted at times when herbicide applications could potentially occur in Georgia vegetable production and are thus

representative of producer practices. Cumulative water as a solvent from irrigation for the five wash off events was 4 to 5 cm (data not shown).

The exponential decay equation [1] effectively described dry and irrigated glyphosate dissipation (Figure 1). First-order-dissipation rate constants (*k*) for glyphosate were significantly less (i.e., slower dissipation) for the dry study at 0.008 than for the irrigated study at 0.933 (Table 3). For glyphosate, DT<sub>50</sub> for the dry study was 84 h, while it was 1 h in the irrigated experiment. Glyphosate concentration dropped to less than 5 mg m<sup>-2</sup> levels by the second irrigation event at 24 HAT. Glyphosate dropped to undetectable levels by the fifth irrigation at 96 HAT (Figure 1) when greater than 4 cm of water had been applied. Glyphosate has negligible photo degradation losses, is tightly adsorbed to soil, and has high water solubility (Senseman 2007). Glyphosate adsorption to clay minerals is pH dependent and fluctuations can occur, depending upon the type of soil saturating cation (McConnell and Hossner 1985). In contrast to the wash off experiments, glyphosate dissipation from LDPE mulch for the dry study was linear and 50 mg m<sup>-2</sup> remained 120 HAT. With the dry study 84 h half-life for glyphosate from these experiments, it would require at least 28 d (eight half-lives) to reach less than 1 mg m<sup>-2</sup> on the LDPE mulch. Glyphosate can be persistent in LDPE mulch as reported by Gilreath and

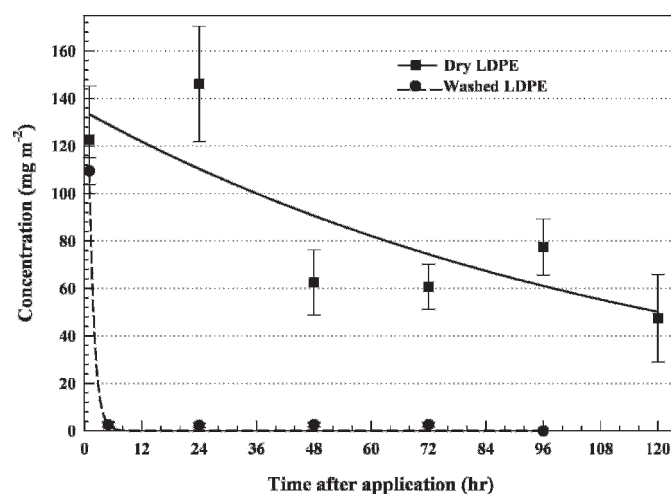


Figure 1. Glyphosate dissipation dry vs. wash off studies for low density polyethylene (LDPE) mulch in Georgia using the exponential decay equation. The line represents the first-order regression equation. Data points are the means of replications with bars indicating the standard error of the mean:

LDPE: dry  $\gamma = 134.5e^{(-0.0082x)}$   $P < 0.0001$   
LDPE: irrigated  $\gamma = 278.4e^{(-0.93x)}$   $P < 0.0001$

Table 3. First-order-dissipation rate constants ( $k$ ) and half-lives ( $DT_{50}$ ) of glyphosate, paraquat, halosulfuron, carfentrazone, and flumioxazin from low density polyethylene (LDPE) mulch for dry and wash off scenarios from experiments conducted in 2003 and 2004.

Herbicide	LDPE	First-order rate constant <sup>a</sup> per event	$DT_{50}$
			h
Glyphosate	Dry	0.008 a <sup>b</sup>	84
	Irrigated	0.933 b	1
Paraquat	Dry	0.022 a	32
	Irrigated	1.88 b	1
Halosulfuron	Dry	0.038 a	18
	Irrigated	0.24 b	3
Carfentrazone	Dry	0.023 a	30
	Irrigated	0.025 a	28
Flumioxazin	Dry	0.0122 a	57
	Irrigated	0.121 b	6

<sup>a</sup> First-order-dissipation rate constants were calculated by nonlinear regression of the herbicide quantity with respect to time (1 to 120 h for dry and 1 to 96 h for wash off after treatment).

<sup>b</sup> Values for each herbicide for first-order-rate constants within a column followed by the same letter are not significantly different at the 5% probability level. General linear models procedures were used with mean separation using 95% asymptotic confidence intervals.

Santos (2004). For their bioassay study with tomato (*Lycopersicon esculentum* L.) in a dry study, they indicated there was enough glyphosate remaining 16 d after application to reduce fresh plant weight by 73%.

First-order-dissipation rate constants ( $k$ ) for paraquat were significantly different for the irrigated (1.88) and dry studies (0.022) (Table 3). Paraquat is a cationic dichloride salt with a water solubility of 620,000 mg L<sup>-1</sup> (Senseman 2007). After the first irrigation application of 1 cm of water, paraquat was undetectable on the LDPE mulch (Figure 2), which was further demonstrated with a 1 h  $DT_{50}$ . Given the high water solubility of paraquat, rapid dissipation will occur with water. As previously noted, paraquat dissipation can also occur via photo degradation (Senseman 2007). With each subsequent 24 h sampling period, paraquat dissipation was reduced stepwise, falling to 10 mg m<sup>-2</sup> at 120 HAT (Figure 2) with a  $DT_{50}$  of 32 h for the dry study. Gilreath et al. (2006)

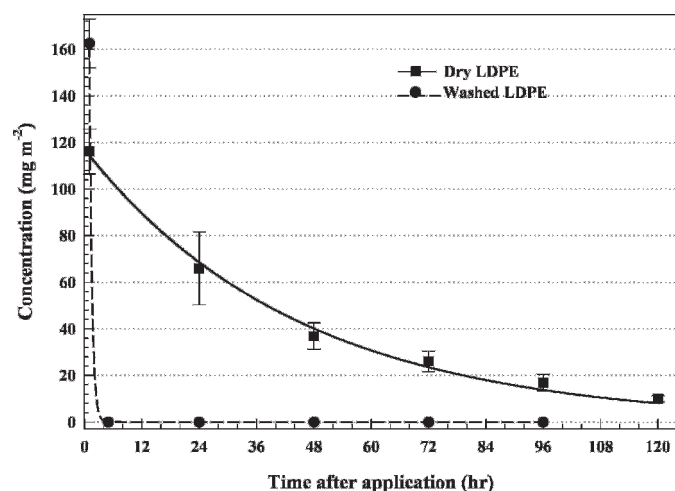


Figure 2. Paraquat dissipation dry vs. wash off studies for low density polyethylene (LDPE) mulch in Georgia using the exponential decay equation. The line represents the first-order regression equation. Data points are the means of replications with bars indicating the standard error of the mean:

LDPE: dry  $\gamma = 117e(-0.022x)$   $P < 0.0001$   
 LDPE: irrigated  $\gamma = 278.4e(-1.88x)$   $P < 0.0001$

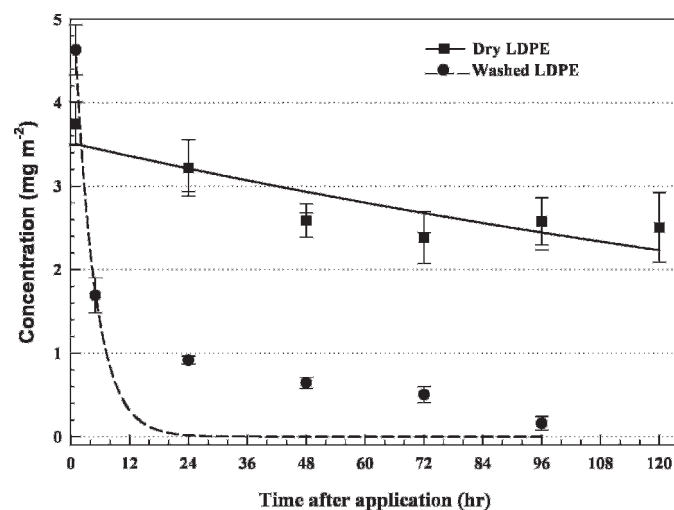


Figure 3. Halosulfuron dissipation dry vs. wash off studies for low density polyethylene (LDPE) mulch in Georgia using the exponential decay equation. The line represents the first-order regression equation. Data points are the means of replications with bars indicating the standard error of the mean:

LDPE: dry  $\gamma = 3.52e(-0.038x)$   $P < 0.0001$   
 LDPE: irrigated  $\gamma = 5.89e(-0.24x)$   $P < 0.0001$

reported similar findings for paraquat on LDPE mulch using a colorimetric analysis procedure.

The exponential decay equation [1] described halosulfuron dissipation for the dry study with a first-order-rate constant ( $k$ ) of 0.038 (Table 3). In the irrigated study, however, the exponential decay equation did not accurately describe halosulfuron dissipation from LDPE mulch, and actually underestimated the levels detected (Figure 3). Halosulfuron dissipation for the irrigated study appeared to be biphasic, with an initial rapid decline, and then little to no removal with each subsequent irrigation event. The first phase of halosulfuron dissipation is chemical hydrolysis and is abiotic in nature, whereas the second phase is microbial dependent. This would explain the biphasic nature for observed dissipation with irrigation. Halosulfuron dissipation in the irrigated study had a first-order-rate constant of 0.24, which was significantly higher

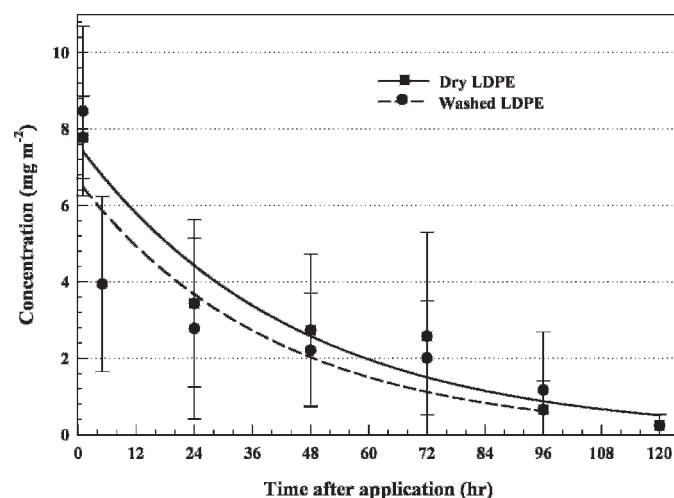


Figure 4. Carfentrazone dissipation dry vs. wash off studies for low density polyethylene (LDPE) mulch in Georgia using the exponential decay equation. The line represents the first-order regression equation. Data points are the means of replications with bars indicating the standard error of the mean:

LDPE: dry  $\gamma = 7.59e(-0.023x)$   $P < 0.0001$   
 LDPE: irrigated  $\gamma = 6.65e(-0.025x)$   $P < 0.0001$



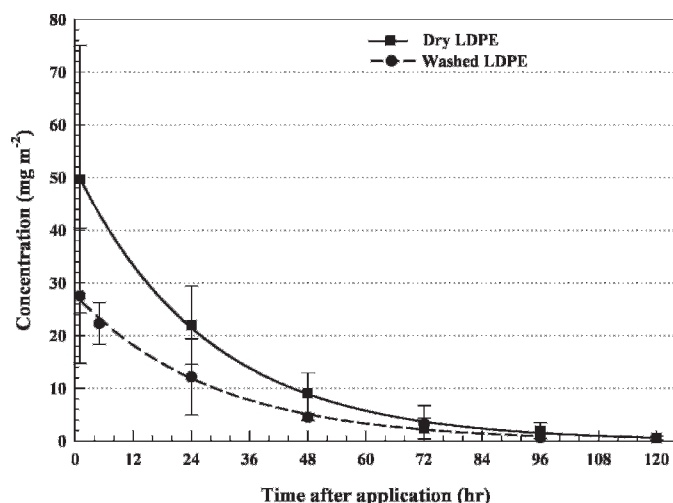


Figure 5. Flumioxazin dissipation dry vs. wash off studies for low density polyethylene (LDPE) mulch in Georgia using the exponential decay equation. The line represents the first-order regression equation. Data points are the means of replications with bars indicating the standard error of the mean:

LDPE: dry  $\gamma = 1.19e(-0.0122x)$   $P < 0.0004$   
 LDPE: irrigated  $\gamma = 0.76e(-0.121x)$   $P < 0.006$

than that in the dry study. Halosulfuron is a weak acid with negligible photo-degradation losses (Senseman 2007). Halosulfuron has exhibited hysteresis in higher organic matter Japanese soils (Dermiyati and Yamamoto 1997). Given this previously noted hysteric soil affect, we suspect halosulfuron is behaving similarly when applied to LDPE mulch. Halosulfuron dissipation was linear and varied by less than  $1.1 \text{ mg m}^{-2}$  from initial application with  $3.5 \text{ mg m}^{-2}$  at 1 HAT to  $2.4 \text{ mg m}^{-2}$  at 120 HAT for the dry study (Figure 3).

Dissipation of carfentrazone was well described by the exponential decay equation [1] with first-order-rate constants of 0.023 and 0.025, and  $DT_{50}$  values of 30 and 28 h for the dry and wash off studies, respectively (Table 3). Sampling of the dry and irrigation studies indicated nearly identical dissipation curves (Figure 4). Initial carfentrazone concentrations on the LDPE mulch were  $7.8$  to  $8.4 \text{ mg m}^{-2}$  at 1 HAT. With each subsequent sampling at 24, 48, 72, and 96 HAT, carfentrazone concentrations were not differing by more than  $0.4 \text{ mg m}^{-2}$  for samples of the dry and wash off LDPE mulch. Carfentrazone water solubility is  $12,000 \text{ mg L}^{-1}$  and increases with temperature; it does not photo-degrade, is non-volatile, and is not adsorbed to soil, but is lost via microbial break down (Senseman 2007).

Variation in flumioxazin chemical behavior has been noted in soil experiments (Ferrell and Vencill 2003), exhibiting adsorption and hysteresis in soil (Ferrell et al. 2004).

Flumioxazin has negligible photodecomposition but does have variable half-lives, which are soil pH dependent (Senseman 2007). First order-rate constants of 0.0122 for the dry study and 0.121 for the irrigation experiment were significantly different from each other (Table 3). The exponential decay equation [1] effectively described the dissipation of both scenarios (Figure 5). The  $DT_{50}$  for the wash off experiment was 6 h, with flumioxazin levels undetectable by 24 HAT. The  $DT_{50}$  of 57 h for the dry experiment indicated that flumioxazin was persistent on the LDPE mulch. This could lead to critical efficacy and injury issues if a grower transplants vegetables onto flumioxazin treated LDPE mulch.

For  $^{14}\text{C}$ -labeled paraquat, flumioxazin, and halosulfuron, the variables for herbicide rate and temperature and herbicide rate by temperature were not significant (Table 4). Therefore, data was combined for presentation across time for these herbicides. Total recovery varied by herbicide but ranged from 66.8 to 91.4%.

For  $^{14}\text{C}$ -labeled glyphosate, there was an initial pulse with water at 6 HAT at 3 and 11 ppm, of 64.2 and 77.2%, respectively (Table 4). For subsequent washes at 24 and 48 HAT, assayed  $^{14}\text{C}$ -glyphosate fell to less than 1.9% for both concentrations. By 96 HAT,  $^{14}\text{C}$ -glyphosate had fallen to less than 0.5% (data not shown).  $^{14}\text{C}$ -paraquat recovery was 73% at 6 HAT, but was nondetectable at 24, 48, and 96 (data not shown) HAT. For glyphosate and paraquat, the radio-labeled experiment results were similar to the analytical analysis performed for samples from the field trials.  $^{14}\text{C}$ -flumioxazin and  $^{14}\text{C}$ -halosulfuron exhibited an initial pulse of 70.7% and 88.9% at 6 HAT, respectively. They then fell to 1.7% or less for recovery at 24, 48, and 96 HAT (data not shown).

These studies indicated that glyphosate and paraquat dissipation was rapid from LDPE mulch when irrigation water was used as a solvent. Total flumioxazin dissipation required at least two irrigation events to reach nondetectable levels (Figure 5). Halosulfuron and carfentrazone were detectable even after five wash off events, indicating that some type of adsorption, or physical trapping within the matrix, may be occurring with the LDPE mulch, with subsequent release with each wash off event (Figures 3 and 4). Similar results to the field studies were observed with the  $^{14}\text{C}$ -glyphosate,  $^{14}\text{C}$ -paraquat,  $^{14}\text{C}$ -flumioxazin, and  $^{14}\text{C}$ -halosulfuron experiments.

Glyphosate, paraquat, halosulfuron, carfentrazone, and flumioxazin were all detectable at efficacious levels on the LDPE mulch at 120 HAT for the dry studies. These studies indicate that producers must be very conscious of the contact herbicide they apply between crops in LDPE mulch production. They must also understand that using water as

Table 4.  $^{14}\text{C}$ -herbicide wash off from low density polyethylene mulch over time in laboratory experiments.<sup>a,b,c</sup>

	Glyphosate				
Time of wash	3 ppm	11 ppm	Paraquat	Flumioxazin	Halosulfuron
HAT	% of applied				
6	64.2 a	77.2 a	73 a	70.7 a	88.9 a
24	1.5 b	1.9 b	ND b	1.7 b	1.5 b
48	1.2 b	1.1 b	ND b	1.1 b	0.5 b
Total	66.8	80.1	73	73.5	91.4

<sup>a</sup> Abbreviations: HAT, hours after treatment.

<sup>b</sup> The variables for herbicide rate and temperature, and herbicide rate by temperature were not significant therefore data was combined for presentation across time for flumioxazin, halosulfuron, and paraquat.  $^{14}\text{C}$ -herbicides were applied with commercially formulated products.

<sup>c</sup> Numbers indicate the percent of washed off of the LDPE mulch for each  $^{14}\text{C}$ -herbicide.

a dissipation mechanism may not totally remove the potential for herbicidal injury to vegetable transplants, and that failure to do so could result in significant plant injury and potential crop failure.

## Sources of Materials

<sup>1</sup> Low density polyethylene mulch, Pliant Corp., 1475 Woodfield Road, Suite 700 Schaumburg, IL 60173.

<sup>2</sup> Gramoxone Inteon™, paraquat, EPA Reg. No. 100-1217, Syngenta Crop Protection, Inc., Ag Products, P.O. Box 18300, Greensboro, NC 27419. 35 P.

<sup>3</sup> Roundup Weathermax™, glyphosate, EPA Reg. No. 524-537, Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, MO 63167. 23 P.

<sup>4</sup> Aim 2EC™, carfentrazone-methyl, EPA Reg. No. 279-3241, FMC Corp., Agriculture Products Group, 1735 Market St. Philadelphia, PA 19103. 17 P.

<sup>5</sup> Sandea™, halosulfuron-methyl, EPA Reg. No. 10163-254, Gowan Co., P.O. Box 5569, Yuma, AZ 85366-5569. 21 P.

<sup>6</sup> Valor™, flumioxazin, EPA Reg. No. 59639-99, Valent USA Corp., 1333 N. California Blvd. Suite 600, Walnut Creek, CA 94596. 19 P.

<sup>7</sup> Teejet 11002 flat-fan nozzle, Spraying Systems Co., North Ave., Wheaton, IL 60189.

<sup>8</sup> Brown glass bottles, 250 ml, C&G Containers, 152 Easy Street, Lafayette, LA 70506.

<sup>9</sup> Extraction supplies by Fisher Scientific International Inc., Liberty Lane, Hampton, NH 03842.

<sup>10</sup> Analytical supplies, equipment, and software by Waters Corporation, 34 Maple Street, Milford, Massachusetts 01757.

<sup>11</sup> SigmaPlot for Windows version 8.0., SPSS Inc., 233 South Wacker Dr., Chicago, IL 60611.

<sup>12</sup> Technical grade <sup>14</sup>C-glyphosate, American Radiolabeled Chemicals, Inc., 11624 Bowling Green Drive, St. Louis, MO 63146.

<sup>13</sup> Technical grade <sup>14</sup>C-paraquat, supplied by Syngenta Corp., 2200 Concord Pike, P.O. Box 8353, Wilmington, DE 19803-8353.

<sup>14</sup> Technical grade <sup>14</sup>C-flumioxazin, supplied by Valent U.S.A. Corp., 1170 West Shaw Ave., Suite 103, Fresno, CA 93711.

<sup>15</sup> Technical grade <sup>14</sup>C-halosulfuron supplied by Monsanto Comp., 800 N Lindbergh Blvd., St Louis, MO 63167.

<sup>16</sup> Scintsafe 30% scintillation fluid, Fisher Scientific International Inc., Lane Hampton, NH 03482.

<sup>17</sup> Beckmann LS 6500 Liquid Scintillation Spectrometer, Beckman-Coulter Inc., 4300 N. Harbor Blvd., Fullerton, CA 92834.

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